

Evaluation of Linter Cellulose as an Alternative Raw Material for Tissue Paper Production

Procjena linter celuloze kao alternativne sirovine za proizvodnju upijajućeg papira

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ABSTRACT • The study was carried out to evaluate Linter Cellulose (LC) as an alternative raw material for tissue paper production. Since LC is generally dark brown in color, it must be bleached before being used in tissue paper production. Bleaching process was applied to LC after impurities and oils were removed. LC was bleached in 9 different conditions with sodium hypochlorite (NaClO). The optical and physical properties of LC were measured in accordance with relevance standards in order to determine optimum bleaching condition. The best results in the optical properties were obtained by bleaching with 12 % NaClO. The whiteness, brightness, and yellowness values were found as 67.54, 64.39, and 6.20, respectively. The physical properties of bleached LC were not suitable for tissue paper production. For this reason, LC and wood fibers (WF) were mixed at certain rates to produce tissue paper. The physical and optical properties of the paper obtained from the mixtures were analyzed to determine the optimum mixing ratio. The results showed that 40 % LC and 60 % WF mixtures can be used in tissue paper products. The important physical properties for tissue paper were Water Retention Value (WRV) and Water Absorption Time (WAT) and these values were found as 293.6 g·m⁻² and 1.67 s. WRV and WAT of LC were found to be better than those of WF (267 g·m⁻² and 2.62 s). As a result, when considering the shortage of pulp and paper raw material, the use of LC in tissue paper production would contribute significantly to procuring the raw material and providing economic production.

Keywords: Linter cellulose, bleaching, sodium hypochlorite, tissue paper.

SAŽETAK • Istraživanje je provedeno radi procjene linter celuloze (LC) kao alternativne sirovine za proizvodnju upijajućeg papira. Budući da je LC tamnosmeđe boje, prije uporabe za proizvodnju upijajućeg papira potrebno ga je izbijeliti. Procesi izbijeljivanja LC-a primijenjeni su nakon uklanjanja nečistoća i ulja. LC je izbijeljen natrijevim hipokloridom (NaClO) pri devet različitih uvjeta. Izmjerena su optička i fizikalna svojstva LC-a u skladu s odgovarajućim standardima kako bi se odredili optimalni uvjeti izbijeljivanja. Najbolji rezultati optičkih svojstava dobiveni su izbijeljivanjem 12-postotnim NaClO. Vrijednost bjeline iznosila je 67,54 %, sjajnosti 64,39 % i žutila 6,20 %. Fizikalna svojstva izbijeljenog LC-a nisu prikladna za proizvodnju upijajućeg papira. Stoga je LC pomiješan s drvnim vlakancima (WF) u određenom omjeru kako bi se dobila sirovina prikladna za proizvodnju upijajućeg papira. Fizikalna i optička svojstva papira proizvedenoga od pripremljene smjese analizirana su radi određivanja optimalnog omjera miješanja LC-a i WF-a. Rezultati su pokazali da je smjesa od 40 % LC-a i 60 %

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WF-a može upotrebljavati za izradu proizvoda od upijajućeg papira. Važna fizikalna svojstva upijajućeg papira jesu sposobnost zadržavanja vode (WRV) i vrijeme upijanja vode (WAT). Za proizvedeni upijajući papir izmjerena je vrijednost WRV-a od 293,6 g·m⁻² i WAT-a od 1,67 s. Utvrđeno je da su vrijednosti WRV-a i WAT-a za LC bolje nego vrijednosti za WF (267 g·m⁻² i 2,62 s). Kada se uzme u obzir nedostatak sirovine za proizvodnju celuloze i papira, može se reći da bi upotreba LC-a za proizvodnju upijajućeg papira mogla znatno pridonijeti lakšoj nabavi sirovina i ekonomičnosti proizvodnje.

Ključne riječi: linter celuloza, izbjeljivanje, natrijev hipoklorit, upijajući papir

1 INTRODUCTION

1. UVOD

Cellulose, the raw material of the paper, is obtained from wood and non-wood plants. Due to the use of wood raw materials in different industries (particleboard, plywood, furniture etc.), it has become an expensive raw material. In addition to this, since the process of obtaining wood takes a very long period of time, cellulose production from annual plants has become more attractive (Erdem, 2010). Cotton, one of these annual plants, is primarily grown as textile raw material. Linter is obtained as a by-product from the cotton seed. When compared with wood, cellulose can be more easily obtained from linter. Besides, it is also easier to bleach linter than wood pulps.

The decrease in the availability of raw materials for pulp and paper production has led papermakers to search for new raw material resources. Several studies have been carried out to discover these resources (Chandra, 1998; Tutus and Cicekler, 2016; Comlekcioglu *et al.*, 2016). As an alternative to wood-based raw materials, linter cellulose is an important raw material resource for pulp and paper production. Linter is an important by-product of the textile industry. Cotton linter is the short fiber that cannot be used in the textile process. In order to be used in oil production, cotton seed must be separated from its seed by special cutting methods. After special cutting methods, first and second cut linters are obtained from separated fibers. Cellulose content, color, fiber dimension, and contaminants are important to determine the quality of linter cellulose (LC). Linter has an excess of 80 % of holocellulose, and more than 75 % of it is alpha-cellulose (Dogmaz, 1994; Sczostak, 2009; Morais *et al.*, 2013). LC was first applied in regenerated cellulose production. Also, LC is used in the production of cellulose esters such as nitro cellulose and cellulose acetate (Ward *et al.*, 1965).

The type raw material is one of the most important factors affecting paper quality. Chemical components and fiber properties of wood differ from species to species. For this reason, the characteristics of the pulps produced in certain pulping conditions depend on the wood species (Perez and Funchon, 2003; Shackford, 2003). Softwood pulps are used to produce stronger paper. These pulps are often used as reinforcing pulp in paper production. On the other hand, hardwood pulps are preferred for producing smooth and high-quality writing paper (Chauhan *et al.*, 2011; Gulsoy and Tufek, 2013).

Bleaching is a chemical process applied to enhance the brightness of cellulosic materials. It is possible to increase the service and usage area of the paper

with the bleaching process (Reeve, 1996). The main purpose of the bleaching process is to modify and/or remove the lignin and lignin degradation products, extractive substances, metal ions, non-cellulosic carbohydrate components and any coloring materials in the paper poultry by using appropriate chemical substances and systems (Singh, 1978). Sodium hypochlorite (NaClO) is stable above pH 10 (Cardamone and Marmer, 1995). It is a very cheap oxidizer, with higher redox potential than hydrogen peroxide, and bleaches rapidly at room temperature (Karmakar, 1999; Ibrahim *et al.*, 2010).

Tissue paper is produced by a paper machine that has a single large steam heated drying cylinder (yankee dryer) fitted with a hot air hood. The raw material is paper pulp. The Yankee cylinder is sprayed with adhesives to make the paper stick. Creping is done by the Yankee's doctor blade that is scraping the dry paper off the cylinder surface. The crinkle (crêping) is controlled by the strength of the adhesive, geometry of the doctor blade, speed difference between the Yankee and final section of the paper machine and paper pulp characteristics (Paulapuro, 2000).

Generally, LC has been burned for energy production in the world. However, there is little to no information on the application of this resource for tissue paper production. The objective of this study was to evaluate LC for tissue paper production in the mixture with wood fibers.

2 MATERIALS AND METHODS

2. MATERIJALI I METODE

2.1 Materials

2.1. Materijali

This study was performed at the Kahramanmaraş Sutcu Imam University Faculty of Forestry, Pulp, and Paper Production Laboratory. LC was taken from Pakmil Oil and Cotton Industry Enterprises Inc., in Adana-Turkey and its fiber length and viscosity values are 2.95-3.00 mm and 1300-1350 cp, respectively. The bleached wood pulps, containing 70 % of short fibers (hardwood) and 30 % of long fibers (softwood), were supplied from Kombassan Paper Mill. Chemicals were supplied by Merck (Darmstadt, Germany). Raw material was prepared and physical and optical properties of tissue paper were determined according to the relevant standard methods.

2.2 Preparation of LC pulps

2.2. Priprema LC pulpe

Firstly, LCs was cleaned from rough and non-fibrous contamination. Then, it was kept into cold water

(24 h) and hot water (4 h) in order to remove impurities and oils. Alkali extraction removed a large part of the hemicellulose from linter fibers and decreased the content of the charged groups (Lund *et al.*, 2012). Before bleaching of linter cellulose, alkali extraction was applied at three different rates 8 %, 10 %, and 12 %. After alkali extraction, LC was beaten in a hollander beater to 40 ± 5 °SR freeness, according to TAPPI standard T200 sp-96. All LC pulps were screened on a 0.15 mm slotted screen to remove non-fibrous matters. Test papers were produced from these LC pulps in order to determine optimum alkali extraction condition. According to the results, 10 % alkali extraction gave the best result in terms of the yield and optical properties. These pulps were subjected to NaClO bleaching processes.

2.3 Bleaching of LC pulps

2.3. Izbjeljivanje LC pulpe

LC pulps were bleached with NaClO in 9 different conditions given in Table 1. Time and temperature were kept constant, while NaClO rate and consistency were changed during bleaching processes.

After preparing the bleaching liquors given in Table 1, the pulps were placed in polyethylene bags. Then, the mixtures were put in a water bath, where the temperature was controlled by a thermostat. Fig. 1 presents the stages of the bleaching process. At the end of bleaching, the pulps were pressed up to 20-25 % dryness. The values of whiteness, brightness, and yellowness of the pulps were measured by a color-measuring instrument Datacolor Elrepho in accordance with applicable standards.

After bleaching, the LC pulps were taken out from the water bath and washed with hot and cold water until chemicals were completely removed from the pulp.

Table 1 NaClO bleaching conditions of Linter Cellulose
Tablica 1. Uvjeti izbjeljivanja linter celuloze uz pomoć NaClO

Bleaching Number Redni broj izbjeljivanja	NaClO Charge Udjel NaClO %	Consistency Konzistencija %	Temperature Temperatura °C	Time Vrijeme min
1	8	8	60	60
2	8	12	60	60
3	8	16	60	60
1	12	8	60	60
2	12	12	60	60
3	12	16	60	60
1	16	8	60	60
2	16	12	60	60
3	16	16	60	60

2.4 Tissue paper production with bleached linter cellulose and wood fiber

2.4. Proizvodnja upijajućeg papira od izbjeljene linter celuloze i drvnih vlaknaca

Test papers were produced from bleached LC and the optical properties of these papers were analyzed. Bleached LC pulps with 12 % NaClO at 8 % consistency gave the best results in the optical properties among 9 different bleaching levels. The physical properties of bleached LC were not suitable for tissue paper production. For this reason, LC and wood fibers (WF) were mixed at certain rates to produce tissue paper given in Table 2. As shown in the table, tissue paper was made using 11 different mixture rates. Ten hand-sheets per tested sequence, with the grammage of 30 ± 5 (g·m⁻²), were prepared using a British Sheet Former according to TAPPI T 205 sp-02.

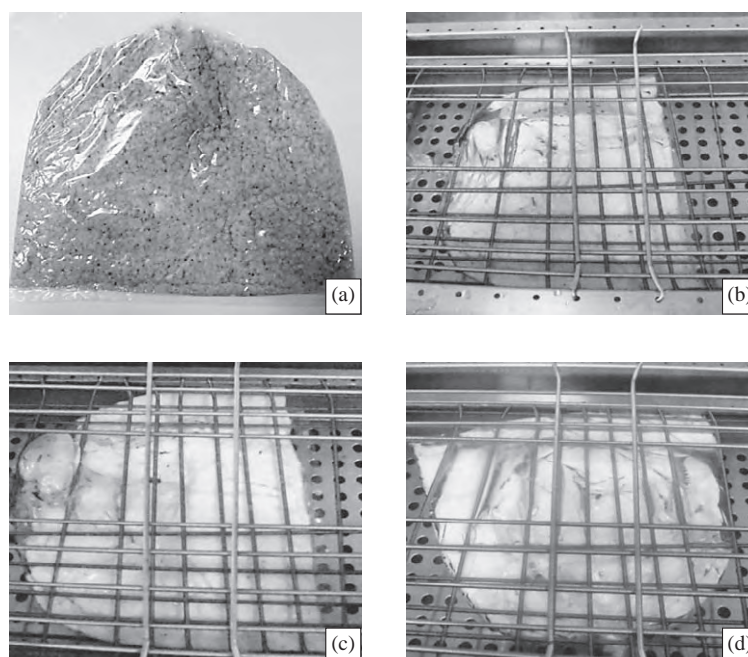


Figure 1 Bleaching stages: before (a), after 15 min (b), after 30 min (c), after 60 min (d)

Slika 1. Prikaz faza izbjeljivanja: a) prije izbjeljivanja, b) 15 minuta nakon izbjeljivanja, c) 30 minuta nakon izbjeljivanja, d) 60 minuta nakon izbjeljivanja

Table 2 Mixing rates of LC and wood fiber**Tablica 2.** Omjeri miješanja linter celuloze i drvnih vlakana

Mixture No / Broj smjese	Linter cellulose / Linter celuloza %	Wood fiber / Drvna vlakanca %
1	0	100
2	10	90
3	20	80
4	30	70
5	40	60
6	50	50
7	60	40
8	70	30
9	80	20
10	90	10
11	100	0

Table 3 Tests applied on tissue paper and applicable standards**Tablica 3.** Provedeno ispitivanje upijajućeg papira i primijenjeni standardi

Physical and optical properties <i>Fizikalna i optička svojstva</i>	Napkin <i>Ubrus</i>	Paper towel <i>Papirnati ručnik</i>	Toilet paper <i>Toaletni papir</i>
Grammage / gramaža, g·m ⁻²	ISO 12625	ISO 12625	ISO 12625
Moisture content / sadržaj vode, %	ISO 12625	ISO 12625	ISO 12625
Whiteness / bjelina (ISO)	ISO 11476	ISO 11476	ISO 11476
Brightness / sjajnost (ISO)	ISO 2470	ISO 2470	ISO 2470
Yellowness / žutilo (ISO)	ISO 5631	ISO 5631	ISO 5631
Thickness / debljina, µm	ISO 12625	ISO 12625	ISO 12625
Bulkiness / obujmnost, g·cm ⁻³	ISO 287	ISO 2470	ISO 12625
Density / gustoća, g·cm ⁻³	ISO 287	ISO 2470	ISO 12625
Breaking length / duljina lomljenja, m	ISO 1924/2	ISO 1924/2	ISO 12625
Water absorption time / vrijeme upijanja vode, s	ISO 12625	ISO 12625	ISO 12625
Water retention value / vrijednost zadržavanja vode, g·m ⁻²	ISO 12625	ISO 12625	ISO 12625

Wood fibers used in this study consist of hardwood (70 %) and softwood (30 %) fibers. They were also beaten in a Hollander beater to 40±5 °SR before being mixed with bleached LC pulps.

2.5 Determining physical and optical properties of tissue paper

2.5. Određivanje fizikalnih i optičkih svojstava upijajućeg papira

The test papers were conditioned at 23±1 °C and 65 % relative humidity in the conditioning room in accordance with TAPPI T 402 om-88 standard. Then, they were prepared for physical and optical tests. Tests were performed according to the standards given in Table 3.

Regression analysis was performed to determine the effect of LC on physical and optical test results of the paper obtained from WF and LC mixtures, and R^2 values were calculated and plotted in the figures bellow.

3 RESULTS AND DISCUSSION

3. REZULTATI I RASPRAVA

The optical properties and yields of LC pulps subjected to alkali extraction are presented in Table 4.

According to Table 4, as the alkali charge increased, the optical properties of the LC pulps increased at first, then decreased. Alkali extraction re-

Table 4 Optical properties and yields of LC pulps after alkali extraction**Tablica 4.** Optička svojstva i prinos pulpe LC-a nakon ekstrakcije lužinom

NaOH charge / Udjel NaOH, %	8 %	10 %	12 %
Whiteness / Bjelina (ISO)	37.09	41.10	40.22
Brightness / Sjajnost (ISO)	29.63	33.66	33.37
Yellowness / Žutilo (ISO)	29.25	25.85	27.35
Yield / Prinos, %	93.81	89.99	88.62

moves a large amount of hemicellulose and causes the yield loss. For this reason, the yields decreased with increasing alkali charge. As 10 % NaOH charge resulted in the best optical properties, these pulps were subjected to NaClO bleaching process.

Bleached LC handsheets, with the grammage of 70±5 (g m⁻²), were prepared to determine optical properties in order to better understand the bleaching efficiency. The yields and optical properties of LC pulps bleached with NaClO are given in Table 5.

As can be seen in Table 5, the best optical properties were obtained from LC pulps bleached with 12 % NaClO. In the same table, pulps bleached at 8 % consistency resulted in the best optical properties. According to these results, pulps bleached with 12 % NaClO at 8 % consistency were used for tissue paper produc-

Table 5 Optical properties and yields of LC pulps bleached with NaClO

Tablica 5. Optička svojstva i prinos pulpe LC-a izbijeljene uz pomoć NaClO

NaClO Charge <i>Udjel NaClO, %</i>	8 %			12 %			16 %		
Pulp properties <i>Svojstva pulpe</i>	Consistency, % <i>Konzistentnost, %</i>			Consistency, % <i>Konzistentnost, %</i>			Consistency, % <i>Konzistentnost, %</i>		
	8%	12%	16%	8%	12%	16%	8%	12%	16%
pH	10.4	10.2	10.1	10.5	10.3	10.2	10.6	10.8	11.0
Viscosity / <i>viskoznost</i> , cm ² ·gr ⁻¹	1013	1086	1105	983	997	1001	956	977	981
Fiber length / <i>duljina vlakana</i> , mm	2.60	2.63	2.66	2.48	2.48	2.50	2.32	2.33	2.40
Whiteness / <i>bjelina</i> (ISO)	76.87	75.91	76.88	76.57	76.25	76.26	75.97	73.06	73.13
Brightness / <i>sjajnost</i> (ISO)	71.38	70.67	71.47	73.47	72.34	72.22	72.23	68.87	68.78
Yellowness / <i>žutilo</i> (ISO)	9.34	9.02	9.20	5.54	6.64	6.92	6.34	7.40	7.79
Yield / <i>prinos</i> , %	85.40	91.60	88.75	85.80	82.80	83.64	81.96	79.96	82.88

Table 6 Optical properties of tissue paper obtained with mixed pulps

Tablica 6. Optička svojstva upijajućeg papira proizvedenoga od različitih smjesa pulpe

Mixture rates, % <i>Omjer smjese, %</i>	Whiteness (ISO) <i>Bjelina (ISO)</i>	Brightness (ISO) <i>Sjajnost (ISO)</i>	Yellow- ness (ISO) <i>Žutilo (ISO)</i>
100 WF	70.99	69.07	3.60
90 WF+10 LC	70.21	68.18	3.85
80 WF+20 LC	69.76	67.58	4.15
70 WF+30 LC	69.24	67.00	4.30
60 WF+40 LC	69.21	66.94	4.32
50 WF+50 LC	68.78	66.33	4.77
40 WF+60 LC	68.73	66.19	4.84
30 WF+70 LC	68.38	65.68	5.26
20 WF+80 LC	68.19	65.39	5.46
10 WF+90 LC	67.59	64.67	5.74
100 LC	67.54	64.39	6.20

tion with WF. As NaClO charge increases, the bleaching yield decreases due to degradation of other carbohydrates, such as cellulose and hemicellulose. The oxidation of cellulose with hypochlorite is non-specific and degradation proceeds most rapidly near a neutral pH (Lewin and Epstein, 1962).

Mixed LC and WF handsheets, with the grammage of 30±5 (g·m⁻²), were produced and optical properties of these handsheets are presented in Table 6.

In Table 6, it can be clearly seen that as LC ratio increased, the whiteness and brightness values decreased and the yellowness value increased. The optical properties of the LC pulps bleached by the above methods were lower than those of WF. Therefore, the brightness and whiteness values of the mixed pulp decreased.

The physical properties of the paper manufactured with mixed pulps are given in Table 7. This table indicates that increased LC ratio in the mixture significantly reduced the breaking length of the paper. This may be due to the fact that WF has longer fibers than LC as mentioned in the introduction. Several researchers found that the fiber length directly affects the physical properties of the paper. This finding led to the conclusion that long fibers are stronger than short fibers (Diaz *et al.* 2007; Beg and Pickering, 2008; Thumn and Dickson, 2013; Tutus and Cicekler, 2016).

In European and international trade, both water absorption time and water retention value represent important parameters for comparison of the tissue product (Anon., 2011; Tutus *et al.*, 2016). When compared with WF, the water retention value increased

Table 7 Physical properties of tissue paper obtained with mixed pulps

Tablica 7. Fizikalna svojstva upijajućeg papira proizvedenoga od različitih smjesa pulpe

Mixture rates, % <i>Omjer smjese, %</i>	Thickness <i>Debljina</i> , µm	Density <i>Gustoća</i> , g·cm ⁻³	Bulkiness <i>Obujmnost</i> cm ³ ·g	Breaking length <i>Duljina lomljenja</i> m	Water absorp- tion time <i>Vrijeme upijanja vode</i> s	Water retention value <i>Vrijednost zadržavanja vode</i> g·m ⁻²
100 WF	103	0.30	3.34	1319.94	2.62	267.50
90 WF+10 LC	104	0.30	3.31	1159.34	2.21	271.80
80 WF+20 LC	106	0.28	3.52	1030.99	1.99	279.70
70 WF+30 LC	108	0.29	3.40	919.23	1.74	288.20
60 WF+40 LC	112	0.29	3.48	750.52	1.67	293.60
50 WF+50 LC	117	0.26	3.90	803.30	1.43	295.30
40 WF+60 LC	124	0.25	3.94	753.18	1.26	301.20
30 WF+70 LC	128	0.25	4.01	377.67	1.07	307.00
20 WF+80 LC	131	0.25	4.08	352.61	0.98	312.50
10 WF+90 LC	131	0.25	3.92	242.20	0.85	316.00
100 LC	135	0.25	3.93	218.68	0.76	320.40

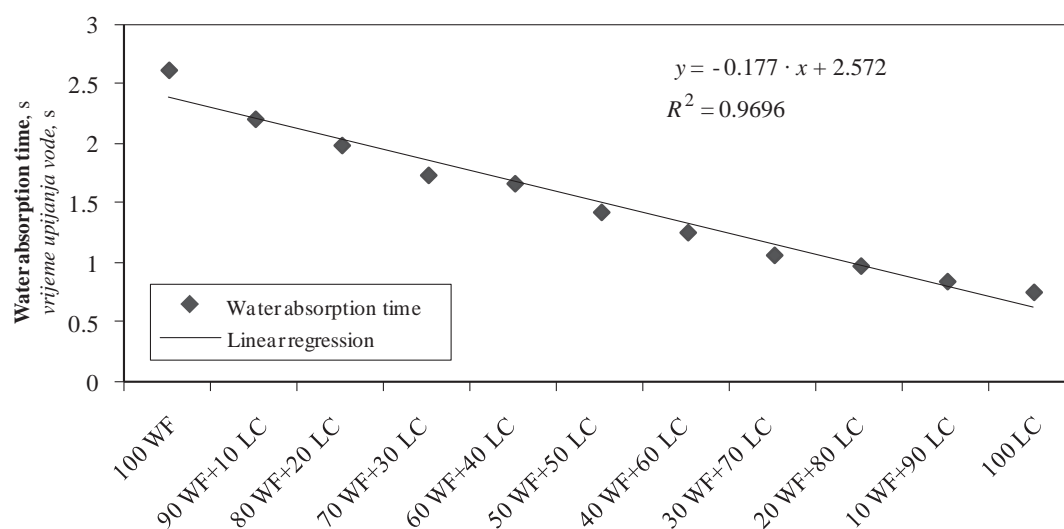


Figure 2 Water absorption times of tissue papers

Slika 2. Vrijeme upijanja vode upijajućih papira proizvedenih od različitih smjesa pulpe

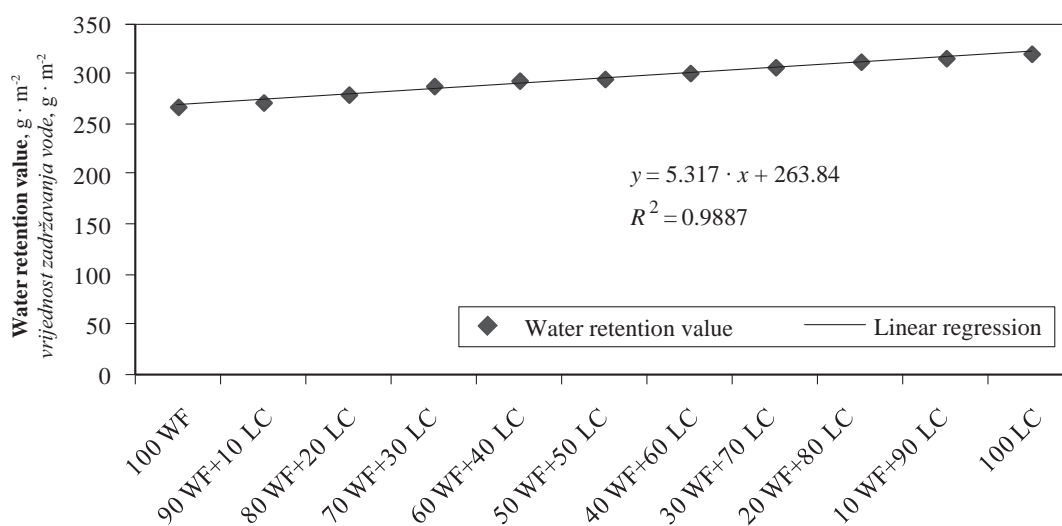


Figure 3 Water retention values of tissue papers

Slika 3. Vrijednosti zadržavanja vode upijajućih papira proizvedenih od različitih smjesa pulpe

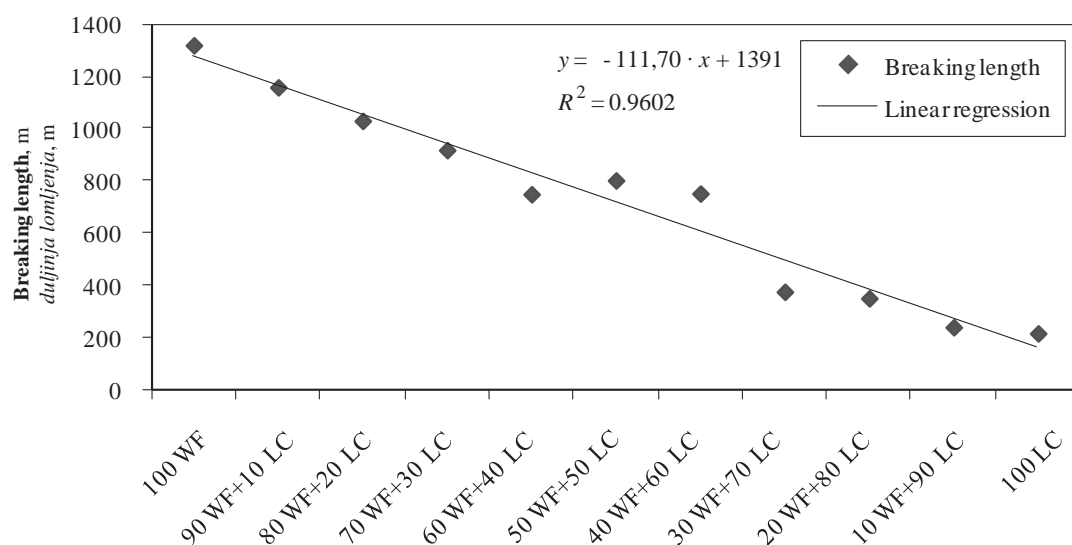


Figure 4 Breaking length values of tissue papers

Slika 4. Duljina lomljenja upijajućih papira proizvedenih od različitih smjesa pulpe

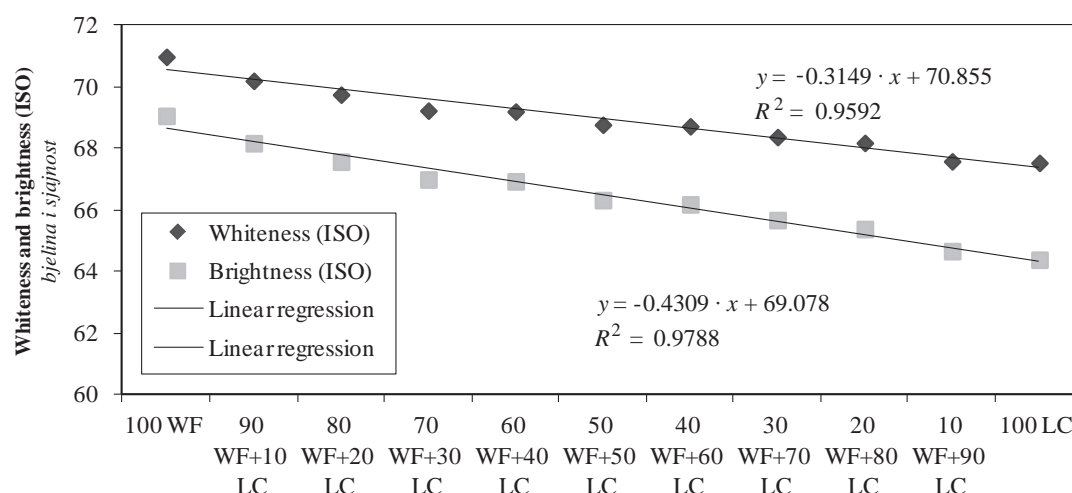


Figure 5 Whiteness and brightness values of tissue papers
Slika 5. Bjelina i sjajnost upijajućih papira proizvedenih od različitih smjesa pulpe

about 120 % and the water absorption time of the tissue paper decreased about 344 % with increasing LC pulp ratio (Table 7). These values have an important role in determining the quality of the tissue paper. On the contrary, the breaking length of the tissue paper reduced with increasing LC pulp ratio.

Fig. 2, 3, 4, and 5 present water absorption time, water retention value, breaking length, whiteness and brightness values of the tissue paper in order to determine the relationship between LC ratios.

Linear correlations with regression coefficients $R^2 = 0.97$, 0.99 , 0.96 , and 0.96 were found for water absorption time, water retention value, breaking length, whiteness and brightness, respectively. It can be obviously seen that there is strong correlation between LC ratios and these values.

4 CONCLUSION

4. ZAKLJUČAK

1. It was determined that the optimal bleaching conditions for LC pulps were 12 % NaClO at 8 % consistency. Using bleached LC pulps, these conditions are suitable for tissue papermaking. These pulps can be used mixed with bleached wood pulps in tissue paper production.

2. LC pulps bleached with NaClO have lower optical properties than bleached WF. The optical properties can be further improved, but the bleaching was performed in mild conditions due to loss yield and degradation of other carbohydrates. On the other hand, some important properties for tissue paper, such as water absorption time and water retention value, were better than those of WF.

3. Some physical and optical properties showed a strong logarithmical correlation with LC pulps ratio. The breaking length, whiteness, brightness and water absorption time decreased with increasing LC pulp ratio, while on the contrary, the water retention values increased.

4. When examining the optical and physical properties of the tissue paper produced with LC and WF mixture, it was determined that tissue paper can be manufactured with 40 % LC and 60 % WF mixture.

5. Evaluation of linter could increase the availability of fibers in countries such as Turkey, where wood resources are limited. The use of linter cellulose in the paper production would be a great contribution to the economy.

6. Turkey has an important potential in the production of linter cellulose. The assessment of this potential will have positive effects on both Turkey's development and its economy.

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